Structures of rhenium(I) complexes with 3-hydroxyflavone and benzhydroxamic acid as O,O -bidentate ligands and confirmation of -stacking by solid-state NMR spectroscopy

Schutte-Smith, Marietjie ; Roodt, Andreas ; Alberto, Roger ; Twigge, Linette ; Visser, Hendrik Gideon ; Kirsten, Leo ; Koen, Renier

Abstract: The synthesis and crystal structures of two new rhenium(I) complexes obtainedutilizing benzhydroxamic acid (BHAH) and 3-hydroxyflavone (2-phenyl-chromen-4-one, FlavH) as bidentate ligands, namely tetraethylammoniumfac-(benzhydroxamato-2O,O0)bromidotricarbonylrhenate(I), (C8H20N)[ReBr(C7H6-NO2)(CO)3],1,andfac-aquatricarbonyl(4-oxo-2-phenylchromen-3-olato-2O,O0)-rhenium(I)–3-hydroxyflavone (1/1), [Re(C15H9O3)(CO)3(H2O)]C15H10O3,3, arereported. Furthermore, the crystal structure of free 3-hydroxyflavone, C15H10O3,4, was redetermined at 100 K in order to compare the packing trends and solid-state NMR spectroscopy with that of the solvate flavone molecule in3.Thecompounds were characterized in solution by1H and13C NMR spectroscopy,and in the solid state by13C NMR spectroscopy using the cross-polarizationmagic angle spinning (CP/MAS) technique. Compounds1and3both crystallizein the triclinic space groupP1 with one molecule in the asymmetric unit, while4crystallizes in the orthorhombic space groupP212121. Molecules of1and3generate one-dimensional chains formed through intermolecular interactions. Acomparison of the coordinated 3-hydroxyflavone ligand with the uncoordinatedsolvate molecule and free molecule4shows that the last two are virtuallycompletely planar due to hydrogen-bonding interactions, as opposed to theformer, which is able to rotate more freely. The differences between the solid-and solution-state13C NMR spectra of3and4are ascribed to inter- andintramolecular interactions. The study also investigated the potential labelling ofboth bidentate ligands with the correspondingfac-99mTc-tricarbonyl synthon.All attempts were unsuccessful and reasons for this are provided.

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Structures of rhenium(I) complexes with 3-hydroxyflavone and benzhydroxamic acid as *O,O′*-bidentate ligands and confirmation of π-stacking by solid-state NMR spectroscopy

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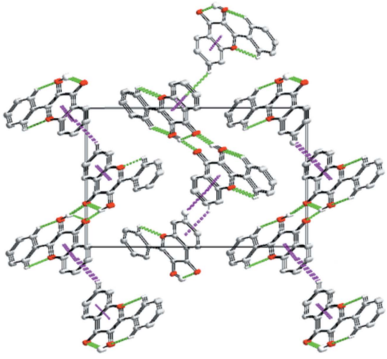
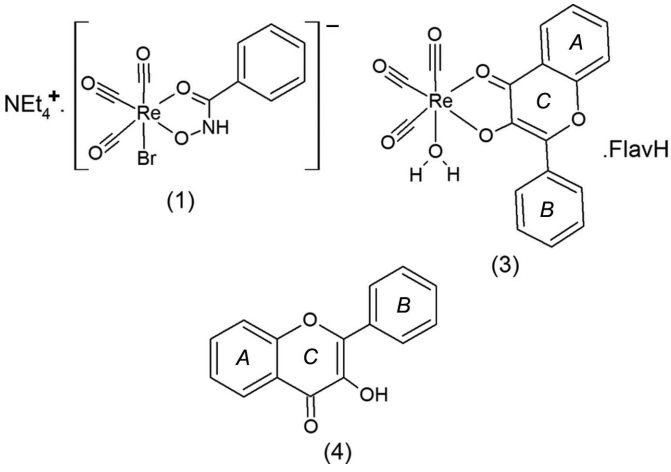
The synthesis and crystal structures of two new rhenium(I) complexes obtained utilizing benzhydroxamic acid (BHAH) and 3-hydroxyflavone (2-phenylchromen-4-one, FlavH) as bidentate ligands, namely tetraethylammonium *fac*-(benzhydroxamato-κ^2O,O')bromidotricarbonylrhenate(I), $(C_8H_{20}N)[ReBr(C_7H_6NO_2)(CO)_3]$, **1**, and *fac*-aquatricarbonyl(4-oxo-2-phenylchromen-3-olato-κ^2O,O')-rhenium(I)–3-hydroxyflavone (1/1), $[Re(C_{15}H_9O_3)(CO)_3(H_2O)]\cdot C_{15}H_{10}O_3$, **3**, are reported. Furthermore, the crystal structure of free 3-hydroxyflavone, $C_{15}H_{10}O_3$, **4**, was redetermined at 100 K in order to compare the packing trends and solid-state NMR spectroscopy with that of the solvate flavone molecule in **3**. The compounds were characterized in solution by ^{1}H and ^{13}C NMR spectroscopy, and in the solid state by ^{13}C NMR spectroscopy using the cross-polarization magic angle spinning (CP/MAS) technique. Compounds **1** and **3** both crystallize in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit, while **4** crystallizes in the orthorhombic space group $P2_12_12_1$. Molecules of **1** and **3** generate one-dimensional chains formed through intermolecular interactions. A comparison of the coordinated 3-hydroxyflavone ligand with the uncoordinated solvate molecule and free molecule **4** shows that the last two are virtually completely planar due to hydrogen-bonding interactions, as opposed to the former, which is able to rotate more freely. The differences between the solid- and solution-state ^{13}C NMR spectra of **3** and **4** are ascribed to inter- and intramolecular interactions. The study also investigated the potential labelling of both bidentate ligands with the corresponding *fac*-^{99m}Tc-tricarbonyl synthon. All attempts were unsuccessful and reasons for this are provided.

1. Introduction

Flavonoids are widely occurring polyphenol compounds of plant origin with carbonyl and hydroxy groups with which they can coordinate to metal ions and form complexes (Kasprzak *et al.*, 2015; Uivarosi *et al.*, 2013; Selvaraj *et al.*, 2014; Naso *et al.*, 2016), many of which have been investigated for their applications in medicine. It has been reported that flavonoids have an abundance of biological activities, including antimicrobial, anti-inflammatory and anticancer, of which many are due to its antioxidant properties (Cushnie & Lamb, 2011; Yamamoto & Gaynor, 2001; Ruela de Sousa *et al.*, 2007; Middleton *et al.*, 2000; Verbeek *et al.*, 2004; Nijveldt *et al.*, 2001). When coordinated to metal ions, promising results were obtained and some compounds show a range of biological activities (Zhou *et al.*, 2001; Chen *et al.*, 2009; Wang *et al.*, 2006; Naso *et al.*, 2010; Durgo *et al.*, 2011; Pereira *et al.*, 2007; Etcheverry *et al.*, 2008; Ferrer *et al.*, 2006).



Hydroxamic acid and its derivatives coordinate to a wide variety of transition metal ions either as monoanionic hydroxamate or dianionic hydroximate *O*,*O*′-bidentate ligands and have also been of interest in applications in medicine (Codd, 2008; Sresutharsan *et al.*, 2017; Adiguzel *et al.*, 2017); it is considered by the research community as an important anticancer therapy candidate (Pal & Saha, 2012). One of the most significant uses of hydroxamic acids, however, is for the treatment of iron-overload disease and, due to some shortcomings of current drugs, much research is focused in this field (Kalinowski & Richardson, 2005; Chaston & Richardson, 2003; Li *et al.*, 2004; Zheng *et al.*, 1985; Tacke *et al.*, 2000; Casellato *et al.*, 1984). Other potential research applications include in rheumatoid arthritis, Crohn's disease and multiple sclerosis (Skotnicki *et al.*, 2003; Puerta & Cohen, 2004). Hydroxamic acids have also been investigated for heavy-metal extraction procedures, nuclear fuel reprocessing, as supramolecular switching devices, as delivery agents for ^{188}Re and for proteomics applications (Szymanowski & Wisniewski, 1996; Taylor *et al.*, 1998; Bodenant *et al.*, 1998; Safavy *et al.*, 1997; Chan *et al.*, 2004; Wang *et al.*, 2006*a*,*b*).



The structure of benzhydroxamic acid, coordinated to a metal centre, has only been reported twice before, *i.e.* coordinated to Zn^{2+} in a bidentate fashion (Göttlicher & Ochsenreiter, 1974) and coordinated to Fe^{3+} in a monodentate mode (Cheng *et al.*, 1999). The crystal structure of 3-hydroxyflavone has been reported before by Etter *et al.* (1986). The molecule also crystallized in the orthorhombic space group $P2_12_12_1$, similar to the structure reported here, but the data were collected at 295 K compared to 100 K.

Several metal centres have been coordinated to the 3-hydroxyflavone ligand in the last few years; from group VII, two Mn^{2+} structures (Kaizer *et al.*, 2007; Grubel *et al.*, 2010) have been reported, but none with the M^+ core (M = Mn, Tc and Re).

The chemistry and possible applications of rhenium- and technetium tricarbonyl complexes in radiopharmacy is well established (Schibli *et al.*, 1998; Alberto *et al.*, 1998, 1999*a*,*b*; Grundler *et al.*, 2004, 2006; Salignac *et al.*, 2003; Jiménez-Pulido *et al.*, 2016; Jia *et al.*, 2016; Ballinger *et al.*, 2004; Leonidova *et al.*, 2014; Alberto, 2003). Several reports in the last ten years have also described the importance of kinetic studies in understanding the possible interaction of potential drugs with their surroundings in the human body (Schutte *et al.*, 2011, 2012; Twala *et al.*, 2015; Brink *et al.*, 2013, 2014; Schutte-Smith & Visser, 2015; Manicum *et al.*, 2015).

In this article, the synthesis and characterization of three *fac*-[Re(Bid)(*X*)(CO)$_3$] (Bid = benzhydroxamate or 3-hydroxyflavonate and $X = Br^-$ or H_2O) complexes are described and three crystal structures are reported, namely *fac*-[NEt$_4$][ReBr(BHA)(CO)$_3$], **1**, *fac*-[Re(Flav)(CO)$_3$(H$_2$O)]·FlavH, **3**, and 3-hydroxyflavone, **4** (see Scheme).

Attempts to label benzhydroxamic acid and 3-hydroxyflavone with ^{99m}Tc were unsuccessful, but possible reasons for this will be discussed.

2. Experimental

2.1. Materials and methods

All the reagents used in the preparations and characterizations were of analytical grade and were purchased from Sigma–Aldrich or Merck, South Africa, unless otherwise stated. The reagents were used without any further purification, the organic solvents were dried and distilled before use and double-distilled water was utilized. Rhenium pentacarbonyl bromide was purchased from Strem Chemicals, Newburyport, MA, USA. The pH of the reaction mixtures was adjusted with HNO_3 solution, while all experiments were performed aerobically, unless otherwise stated.

The IR spectra were recorded at room temperature on a Bruker Tensor 27 Standard System or a PerkinElmer BX II IR spectrometer in the range 4000–370 cm^{-1}. Solid samples were analyzed as KBr pellets.

The HPLC analysis was performed on a Merck–Hitachi L-700 apparatus with a Macherey–Nagel C-18ec reversed-phase column with 5 µm particle size, 100 Å pore size and dimensions 250 × 3 mm. The solvents used were a 0.1% trifluoroacetic acid (TFA) solution in water (solvent A) and HPLC-grade methanol (solvent B). The mobile phase used was a variable TFA gradient: 0–3 min, 100% solvent A; 3–3.1 min, 0–25% solvent B; 3.1–9 min, 75% solvent A, 25% solvent B; 9–9.1 min, 25–34% solvent B, 75–66% solvent A; 9.1–20 min, 34–100% solvent B; 20–25 min, 100% solvent B; 25–25.1 min, 100% solvent B to 100% solvent A; 25.1–30 min, 100% solvent A. The flow rate was 0.5 ml min^{-1} and was monitored at 250 nm. Unless otherwise stated, the TFA gradient was used throughout.

The liquid-state ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a 300 MHz Avance DPX Bruker spectrometer operating at 300.13 and 75.47 MHz for ^{1}H and ^{13}C, respectively, or on a 600 MHz Avance II Bruker spectrometer operating at 600.28 and 150.95 MHz for ^{1}H and ^{13}C, respectively. Acetone-d_6 and chloroform-*d* was used as solvents and are indicated in each case. The chemical shifts (δ) are reported in parts per million (ppm). For chloroform-*d*, the spectra were referenced relative to the tetramethylsilane (TMS) peak and

Table 1
Experimental details.

	1	3	4
Crystal data			
Chemical formula	$(C_8H_{20}N)[ReBr(C_7H_6NO_2)(CO)_3]$	$[Re(C_{15}H_9O_3)(CO)_3(H_2O)]\cdot C_{15}H_{10}O_3$	$C_{15}H_{10}O_3$
M_r	616.52	763.70	238.23
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$	Orthorhombic, $P2_12_12_1$
Temperature (K)	100	100	100
a, b, c (Å)	9.6321 (13), 9.8793 (11), 12.826 (2)	10.5209 (15), 11.9365 (17), 12.4455 (17)	5.3502 (6), 11.3531 (14), 18.063 (2)
α, β, γ (°)	95.806 (10), 108.520 (11), 112.895 (7)	108.277 (7), 102.745 (7), 104.252 (7)	90, 90, 90
V (Å^3)	1030.2 (3)	1361.0 (3)	1097.2 (2)
Z	2	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	7.87	4.53	0.10
Crystal size (mm)	0.38 × 0.25 × 0.11	0.55 × 0.17 × 0.08	0.37 × 0.17 × 0.15
Data collection			
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.109, 0.421	0.417, 0.699	0.980, 0.985
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	18080, 4957, 4720	23222, 6700, 6045	17120, 2621, 2376
R_{int}	0.038	0.038	0.033
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.661	0.674	0.661
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.021, 0.049, 1.04	0.027, 0.060, 1.06	0.034, 0.084, 1.07
No. of reflections	4957	6700	2621
No. of parameters	252	406	165
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	1.78, −1.91	1.40, −2.10	0.21, −0.21
Absolute structure	–	–	Refined as an inversion twin
Absolute structure parameter	–	–	−0.5 (12)

Computer programs: *APEX2* (Bruker, 2008), *SAINT-Plus* (Bruker, 2008), *XPREP* (Bruker, 2008), *SIR97* (Altomare *et al.*, 1999), *WinGX* (Farrugia, 2012), *DIAMOND* (Brandenburg & Putz, 2005) and *SHELXL2018* (Sheldrick, 2015).

for acetone-d_6, the spectra were referenced relative to the solvent peak (2.05 ppm for ^{1}H and 30.83 ppm for ^{13}C). Coupling constants (J) are reported in Hz.

The following bidentate ligand systems were used in this study: benzhydroxamic acid (BHAH) and 3-hydroxyflavone (FlavH).

2.2. Synthesis and crystallization

The starting synthon, *i.e.* *fac*-$[NEt_4]_2[ReBr_3(CO)_3]$, was prepared as described by Alberto *et al.* (1994, 1996).

2.2.1. *fac*-$[NEt_4][ReBr(BHA)(CO)_3]$, 1. Benzhydroxamic acid (BHAH; 0.019 g, 0.140 mmol) was dissolved in water (3 ml, pH 7.5) and *fac*-$[NEt_4]_2[ReBr_3(CO)_3]$ (0.090 g, 0.116 mmol) was added. The solution was stirred for 3 h and then freeze-dried. Colourless block-shaped crystals were collected by dissolving the product in acetonitrile and by vapour diffusion with ether (yield: 0.0623 g, 89%). IR (KBr, cm^{-1}): ν_{CO} = 2004, 1881. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 1.13 (*t*, 12H, J = 4.8 Hz), 2.48 (*q*, 8H, J = 4.8 Hz), 7.60 (*d*, 1H, J = 10.8 Hz), 7.84 (*dd*, 2H, J = 4.8, 10.8 Hz), 8.14 (*d*, 2H, J = 4.8 Hz). ^{13}C NMR (75 MHz, CD_3COCD_3): δ 10.5, 51.5, 127.1, 128.5, 132.4, 135.2, 170.0. ICP–EOS: Re_{calcd} 30.21; Re_{found} 30.83. Analysis calculated (%): C 35.08, H 4.22, N 4.55; found: C 35.69, H 4.19, N 4.69.

2.2.2. *fac*-$[NEt_4][Re(BHA)(CO)_3(H_2O)]$, 2. *fac*-$[NEt_4]_2[ReBr_3(CO)_3]$ (0.50 g, 0.650 mmol) was dissolved in water (20 ml, pH 2.2). Silver nitrate (0.331 g, 1.948 mmol) was added and the solution was stirred for 24 h at room temperature and the AgBr was filtered off. BHAH (0.089 g, 0.650 mmol) was added to the filtrate (adjusted to pH 7) and the resulting solution stirred for 20 h at 80 °C. The reaction mixture was cooled to room temperature and filtered. The water of the filtrate was evaporated off until the product precipitated out (yield: 0.230 g, 86%). IR (KBr, cm^{-1}): ν_{CO} = 2008, 1859. ^{1}H NMR (300 MHz, CD_3COCD_3): δ 7.50 (*d*, 1H, J = 10.4 Hz), 7.78 (*dd*, 2H, J = 4.0 Hz, 10.4 Hz), 8.20 (*d*, 2H, J = 4.0 Hz). ^{13}C NMR (75 MHz, CD_3COCD_3): δ 126.8, 128.1, 133.0, 135.1, 170.5. ICP–EOS: Re_{calcd} 43.88; Re_{found} 43.09. Analysis calculated (%): C 28.30, H 1.89, N 3.30; found: C 28.56, H 1.86, N 3.39.

2.2.3. *fac*-$[Re(Flav)(CO)_3(H_2O)]\cdot$FlavH, 3. Compound **3** was synthesized as described in Schutte *et al.* (2011). Crystals suitable for single-crystal diffractometry were obtained from an aqueous solution of the product (0.300 g, 0.393 mmol) and the data were collected (yield: 0.230 g, 77%). IR (KBr, cm^{-1}): ν_{CO} = 2013, 1885. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (*dd*, 2H, J = 8.6, 1.2 Hz), 7.78 (*d*, 1H, J = 8.3 Hz), 7.74 (*m*, 2H), 7.71 (*dd*,

2H, J = 7.4, 1,0 Hz), 7.24 (*dd*, 1H, J = 8.1, 1.4 Hz), 7.09 (*ddd*, 1H, J = 8.3, 6.1, 1.0). ^{13}C NMR (150 MHz, $CDCl_3$): δ 195.6, 194.8, 194.7, 182.9, 154.9, 154.3, 148.8, 134.5, 132.8, 129.6, 129.3 (×2), 129.2 (×2), 125.3, 123.8, 119.6, 118.2. ICP–EOS: Re_{calcd} 24.39; Re_{found} 24.88. Analysis calculated (%): C 51.91, H 2.75; found: C 52.23, H 2.81.

2.2.4. FlavH, 4. 3-Hydroxyflavone (0.10 g, 0.420 mmol) was dissolved in methanol (50 ml). The solution was stored in a fridge for 2 d. Colourless crystals suitable for single-crystal X-ray crystallography were obtained (yield: 0.084 g, 84%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.25 (*m*, 3H), 7.69 (*ddd*, 1H, J = 8.7, 6.8, 1.6 Hz), 7.57 (*dd*, 1H J = 8.7, 0.9 Hz), 7.53 (*m*, 2H), 7.46 (*m*, 1H), 7.40 (*ddd*, 1H, J = 7.4, 6.8, 0.9 Hz), 7.13 (*s*, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 173.5, 155.4, 144.9, 138.5, 133.6, 131.1, 130.2, 128.6 (×2), 127.8 (×2), 125.5, 124.5, 120.7, 118.3. Analysis calculated (%): C 75.64, H 4.20; found: C 76.21, H 4.18.

2.3. Single-crystal X-ray crystallography

Crystal data, data collection and structure refinement details are summarized in Table 1. The methylene, methyl, aromatic and hydroxy H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C/O—H = 0.99, 0.98, 0.95 or 0.84 Å and U_{iso}(H) = 1.5U_{eq}(C), 1.2U_{eq}(C), 1.2U_{eq}(C) and 1.2U_{eq}(O), respectively. The N—H hydrogen in **1** and the H_2O H atoms in **3** were located from electron-density maps and refined without any constraints. The missing reflections in the FCF file are caused by partial obscuring of the beam stop and due to overflow reflections which are not automatically excluded by the Bruker *APEX2* software (11 reflections for **1**, 10 reflections for **3** and 5 reflections for **4**). Sufficient unique reflections were obtained (4977 for **1**, 6991 for **3** and 2621 for **4**) to yield fully refined structures with 99.6, 97.8 and 99.6% data completeness, respectively.

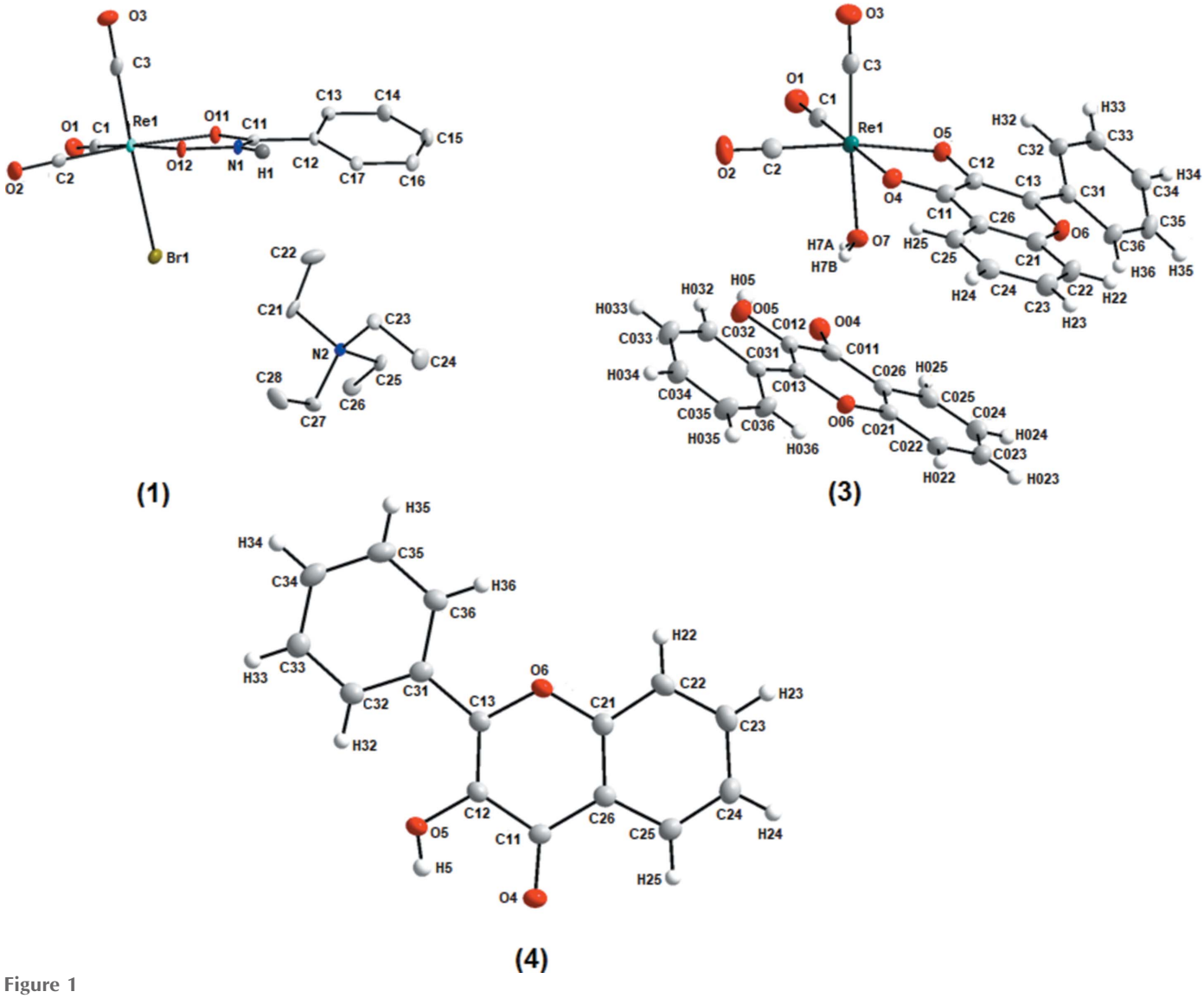


Figure 1
Molecular representations of the crystal structures of *fac*-[NEt_4][ReBr(BHA)$(CO)_3$], **1**, *fac*-[Re(Flav)$(CO)_3(H_2O)$]·FlavH, **3**, and 3-hydroxyflavone, **4**. H atoms have been omitted for clarity. All structures are drawn with displacement ellipsoids at the 50% probability level.

Table 2
Selected bond lengths (Å) and angles (°) for the structures of **1**, **3** and **4**.

1		**3**		**4**	
Re1—C1	1.905 (3)	Re1—C1	1.900 (4)	C11—O4	1.238 (2)
Re1—C2	1.892 (3)	Re1—C2	1.899 (4)	C12—O5	1.350 (2)
Re1—C3	1.889 (3)	Re1—C3	1.892 (4)	C13—C31	1.474 (2)
Re1—Br1	2.6690 (5)	Re1—O7	2.187 (3)	C13—O6	1.370 (2)
Re1—O11	2.1292 (19)	Re1—O4	2.128 (2)	C21—O6	1.361 (2)
Re1—O12	2.1204 (19)	Re1—O5	2.149 (2)		
O11—Re1—O12	76.78 (7)	O4—Re1—O5	76.72 (9)	O4—C11—C12	119.48 (17)
C3—Re1—Br1	177.92 (9)	C3—Re1—O7	174.51 (13)	O5—C12—C11	116.44 (16)
C3—Re1—O11	94.10 (10)	C3—Re1—O5	98.98 (12)	C12—O5—H5	109.5

2.4. Solid-state NMR spectroscopy

The solid-state NMR spectra were collected on a 400 MHz Bruker Avance III spectrometer equipped with a 4 mm VTN multinuclear double resonance magic angle spinning probe, operating at 25 °C. The ^{13}C NMR spectra were recorded at 100.6 MHz, using the cross-polarization magic angle spinning (CP/MAS) technique. A rotating speed of 14000 Hz was used with a contact time of 2 ms, a recycle delay of 5 s and an acquisition time of 33.9 ms. All the spectra were recorded with 2048 scans. The samples were packed in 4 mm zirconia rotors.

2.4.1. *fac*-[Re(Flav)(CO)$_3$(H$_2$O)]·FlavH, 3. ^{13}C CP/MAS NMR (100 MHz): δ 184.7–183.0, 174.2, 157.7, 156.3, 152.6, 152.2, 151.6, 147.4, 139.4, 137.7, 133.1–117.6.

2.4.2. FlavH, 4. ^{13}C CP/MAS NMR (100 MHz): δ 175.8, 156.2, 145.9, 143.0, 133.9, 133.2, 132.1 (×2), 130.4, 130.2, 128.3, 127.2, 125.5, 123.2, 121.0.

3. Results and discussion

3.1. Synthesis and spectroscopy

fac-[NEt$_4$][ReBr(BHA)(CO)$_3$], **1**, *fac*-[Re(BHA)(CO)$_3$(H$_2$O)], **2**, and *fac*-[Re(Flav)(CO)$_3$(H$_2$O)]·FlavH, **3**, were successfully synthesized and characterized by IR, ^{1}H and ^{13}C NMR spectroscopies, while crystals suitable for single-crystal X-ray diffraction was also obtained for **1**, **3** and 3-hydroxyflavone, **4**. ^{99m}Tc labelling efforts were unsuccessful. During the attempted labelling process of benzhydroxamic acid (BHAH), the amount of *fac*-[^{99m}Tc(CO)$_3$(H$_2$O)]$^+$ decreased from 100 to 60% in 30 min after adding the ligand and after a total of 90 min, there was 100% [^{99m}TcO$_4$]$^-$ in the vial. From these experiments it is clear that benzhydroxamic acid acts as an oxidizing agent during this process. At no stage was there any sign of a product forming. Interestingly, synthesis of the rhenium analogue *fac*-[NEt$_4$][ReBr(BHA)(CO)$_3$] was successful and it was possible to determine the crystal structure as well. All attempts to label with FlavH were unsuccessful, possibly due to poor water solubility. The synthesis of the similar rhenium complex was performed at 90 °C for 24 h, indicative of the poor solubility of the ligand.

The carbonyl stretching frequencies of **1**, **2** and **3** are in the same range as other similar *O*,*O*′-donor ligand complexes (Schutte *et al.*, 2011, 2012; Manicum *et al.*, 2018).

3.2. X-ray crystallography

The crystallographic data for *fac*-[NEt$_4$][ReBr(BHA)(CO)$_3$], **1**, *fac*-[Re(Flav)(CO)$_3$(H$_2$O)]·FlavH, **3**, and free 3-hydroxyflavone (FlavH, **4**) are summarized in Table 1.

Compound **1** crystallized in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit. The octahedral geometry around the Re$^{\rm I}$ atom is completed by three facial carbonyl ligands, a bidentate benzhydroxamate ligand and a bromide ligand. A tetraethylammonium cation crystallized with the monoanionic Re$^{\rm I}$ compound. The geometric distortion around the Re$^{\rm I}$ core is best illustrated by the bond angles around the Re$^{\rm I}$ centre, with the largest deviation from 90° found for O11—Re1—O12, with a reported value of 76.78 (7)°. The bond lengths and angles are within the ranges reported for similar structures (Göttlicher & Ochsenreiter, 1974; Cheng *et al.*, 1999; Schutte *et al.*, 2011, 2012; Mokolokolo *et al.*, 2017; Schutte-Smith & Visser, 2015; Manicum *et al.*, 2015, 2018; Twala *et al.*, 2015), as well as for the free molecule (Podlaha *et al.*, 2014). Selected bond lengths and angles for **1** are summarized in Table 2 and the molecular diagram with the atom-numbering scheme is given in Fig. 1.

Several intermolecular (C—H···O and N—H···Br) hydrogen-bond interactions, one C—H···π interaction, one Re—Br···π interaction and one π–π interaction stabilize the solid-state structure of **1**. The geometries of the interactions are summarized in Table 3 and illustrated in Fig. 2. A π–π interaction is observed between the phenyl rings of the benzhydroxamate ligands, with a centroid-to-centroid distance of 3.8385 (6) Å. The cations form links between the Re$^{\rm I}$ anions and, together with the π-interactions and hydrogen-bonding interactions, form a one-dimensional (1D) chain along the *a* axis (N1—H1···Br1), as illustrated in Fig. 2. The phenyl ring of the benzhydroxamate bidentate ligand twists significantly out of the plane, with a dihedral angle of 23.78 (11)° between the planes through Re1/O11/O12/C11/N1 and C12–C17. The O11—C11—C12—C13 torsion angle of **1** is 20.4 (4)°, while in the free molecule (Podlaha *et al.*, 2014), the torsion angle ranges from 7.2 (1) to 21.5 (1)° for the four molecules present.

Compound **3** crystallized in the triclinic space group $P\overline{1}$ with one molecule in the asymmetric unit. Three facial carbonyl ligands, one bidentate 3-hydroxyflavonate ligand and one cordinated water molecule complete the coordination sphere. A free 3-hydroxyflavone molecule crystallized with the Re$^{\rm I}$ compound in the unit cell. The octahedral geometry is

significantly distorted around the Re^{I} core, with O4—Re1—O7 and O5—Re1—O7 angles of 78.55 (10) and 78.02 (10)°, respectively. This could be due to the small O4—Re1—O5 bite angle of 76.72 (9)°. All the bond lengths and angles are in the normal ranges compared to similar compounds (Speier *et al.*, 1990; Balogh-Hergovich *et al.*, 1991; Sun *et al.*, 2014; Annan *et al.*, 1990; Schutte *et al.*, 2011, 2012; Mokolokolo *et al.*, 2017; Schutte-Smith & Visser, 2015; Manicum *et al.*, 2015, 2018; Twala *et al.*, 2015). The Re···Re nonbonding distance is 5.114 (7) Å. Selected bond lengths and angles are reported in Table 2 and the molecular diagram for **3** is illustrated in Fig. 1.

Seven hydrogen-bonding interactions, namely four intramolecular (O—H···O and C—H···O) and three intermolecular (O—H···O and C—H···O) interactions, are observed in **3**. π–π interactions are also observed, *i.e.* O7—H7*A*···*Cg*1, C1—O1···*Cg*2 and C2—O2···*Cg*4 [see Table 3 for ring-centroid (*Cg*) definitions]. Two more π–π interactions are observed between the *C* ring (see Scheme for ring labelling) of the Re^{I} compound and the neighbouring free molecule, and between the *C* rings of two free molecules, with centroid-to-centroid distances of 3.6616 (6) and 3.5435 (5) Å, respectively. The geometries and symmetry operators of the different interactions are given in Table 3, and an illustration of the various interactions is given in Fig. 2. 1D chains are formed along the *b* axis (O7—H7*A*···O04^{f}, O7—H7*B*···O5^{g} and O05—H05···O04; Table 3). The packing of **3** could be stabilized by π–π interactions, with a dihedral angle of 8.68 (13)° between the planes through atoms C21–C26 and C021–C026, and a 0° dihedral angle between the planes through C021–C026 of the two free molecules.

The crystal structure of *fac*-[Re(Flav)(CH_3OH)$(CO)_3$]·-CH_3OH in the space group $P\overline{1}$ has been reported (Schutte *et al.*, 2011). The bond lengths and angles around the Re^{I} centre for these two structures are within the same range. Both structures exhibit hydrogen-bond interactions and π–π interactions. The O5—Re—O4 bite angle is almost the same for the two structures and varies between 76.24 (11) and 76.73 (9)°. The C3—Re—O7 angles are also similar, despite the difference in the coordinated water *versus* methanol ligand in the sixth position, with a value of 174.49 (15)° for **3** and 173.89 (16)° for the methanol-solvated structure. The only significant difference between the two structures is the O6—

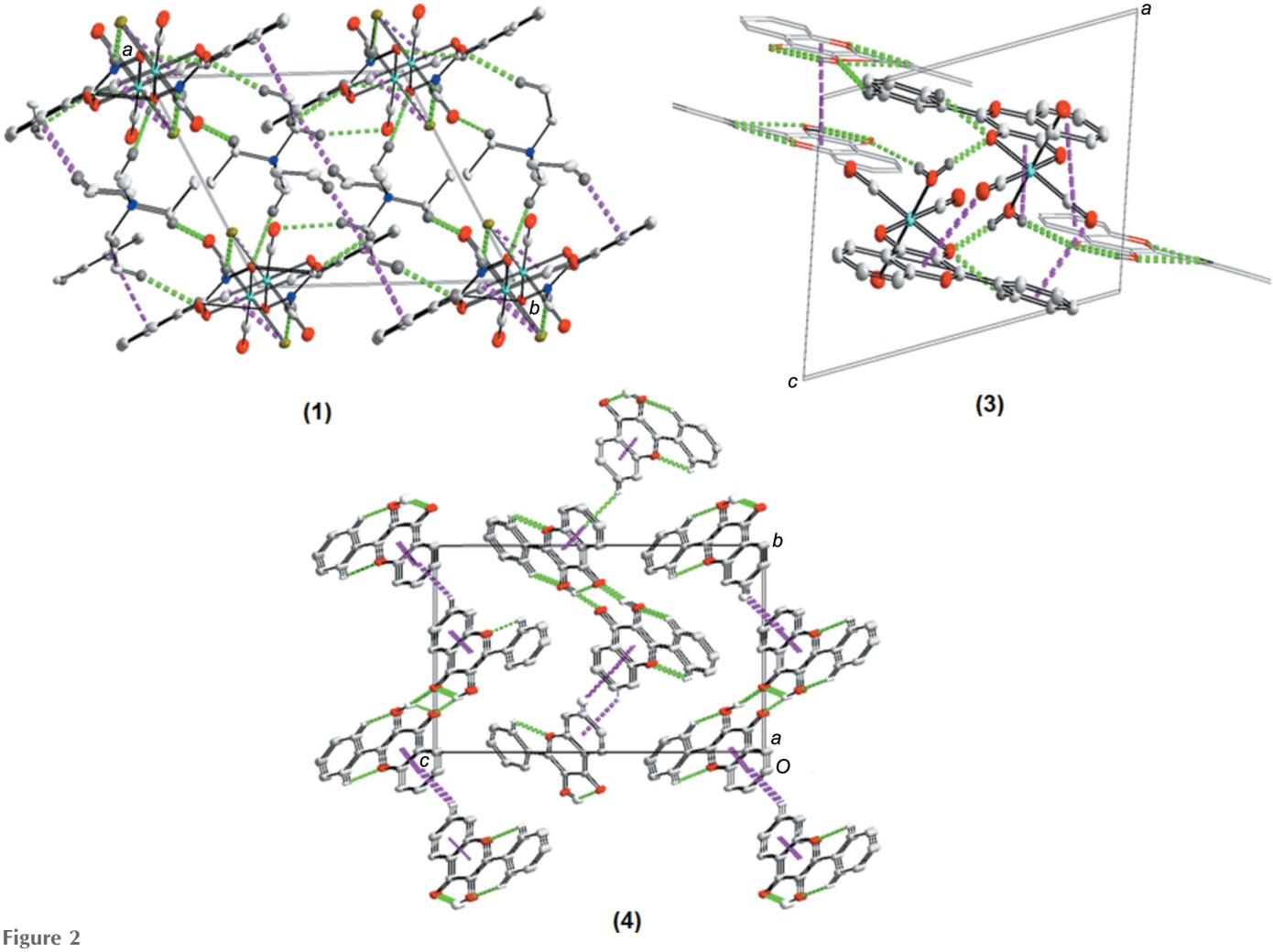


Figure 2
Hydrogen-bond interactions (indicated with green dashed lines) and π–π interactions (indicated in pink dashed lines) observed in **1**, **3** and **4**. H atoms not taking part in the interactions have been omitted for clarity.

Table 3
Summary of the hydrogen-bond interactions and π-interactions observed in **1**, **3** and **4** (Å, °).

For **1**, *Cg*1 is the centroid of atoms Re1, O11, C11, N1 and O12; *Cg*2 is the centroid of atoms C12–C17. For **3**, *Cg*1 is the centroid of atoms Re2, O4, C11, C12 and O5; *Cg*2 is the centroid of atoms O6/C11–C13/C21/C26; *Cg*4 is the centroid of atoms C31–C36. For **4**, *Cg*2 is the centroid of atoms C21–C26.

fac-[NEt_4][$ReBr(BHA)(CO)_3$], **1**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1^{a}	0.91 (4)	2.52 (4)	3.420 (2)	170 (3)
C17—H17···O12^{a}	0.95	2.59	3.385 (3)	142.1
C23—H23*A*···O12^{a}	0.99	2.41	3.388 (3)	170.1
C25—H25*A*···O2^{b}	0.99	2.59	3.111 (3)	112.5
C25—H25*B*···O1^{c}	0.99	2.57	3.520 (4)	161.5
C26—H26*A*···O2^{d}	0.98	2.56	3.520 (4)	166.1
C27—H27*B*···O3^{e}	0.99	2.40	3.286 (3)	148.5

Y—*X*(*I*)	Res(*I*)→*Cg*(*J*)	*X*···*Cg*	*Y*—*X*···*Cg*	*Y*···*Cg*
C22—H22*C*^{a}	[1]→*Cg*2	2.7074 (4)	137.86 (25)	3.496 (5)
Re1—Br1	[1]→*Cg*1	2.9666 (12)	36.575 (8)	1.7908 (10)

fac-[$Re(Flav)(CO)_3(H_2O)$]·FlavH, **3**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O04^{f}	0.65 (5)	2.01 (5)	2.641 (4)	167 (6)
O7—H7*B*···O5^{g}	0.88 (6)	1.81 (6)	2.658 (4)	162 (6)
C35—H35···O05^{h}	0.95	2.46	3.334 (4)	153
O05—H05···O04	0.84	2.12	2.595 (3)	115
C036—H036···O06	0.95	2.35	2.696 (4)	101
C032—H032···O05	0.95	2.21	2.859 (4)	125
C32—H32···O5	0.95	2.41	2.985 (4)	119

Y—*X*(*I*)	Res(*I*)→*Cg*(*J*)	*X*···*Cg*	*Y*—*X*···*Cg*	*Y*···*Cg*
O7—H7*A*	[1]→*Cg*1	2.67 (5)	57 (4)	2.379 (4)
C1—O1^{i}	[1]→*Cg*2	3.500 (3)	110.7 (3)	4.057 (4)
C2—O2^{i}	[1]→*Cg*4	3.377 (4)	92.5 (2)	3.617 (5)

FlavH, **4**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O4	0.82	2.25	2.668 (3)	112
O4—H5···O4^{j}	0.82	1.94	2.703 (3)	154
C36—H36···O6	0.93	2.31	2.657 (3)	102
C32—H32···O5	0.93	2.20	2.853 (4)	127

Y—*X*(*I*)	Res(*I*)→*Cg*(*J*)	*X*···*Cg*	*Y*—*X*···*Cg*	*Y*···*Cg*
C23—H23^{k}	[1]→*Cg*2	2.9430 (8)	140	3.702 (4)

Symmetry code transformations used to generate equivalent atoms: (*a*) $-x, -y, -z+1$; (*b*) $x+1, y+1, z+1$; (*c*) $-x+1, -y+1, -z+1$; (*d*) $-x+1, -y, -z+1$; (*e*) $x+1, y, z+1$; (*f*) $-x+1, -y, -z+1$; (*g*) $x, y, z-1$; (*h*) $x+1, y+1, z$; (*i*) $-x+1, -y, -z+1$; (*j*) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (*k*) $x-\frac{1}{2}, -y+\frac{5}{2}, -z+1$.

C13—C31—C36 torsion angle; in the methanol-solvated structure, the 'twist' of the *B* ring of the flavone ligand is not that large, with a reported value of 6.0 (6)°, while the phenyl ring in the structure reported here 'twists' considerably, with a value of 24.0 (5)°.

If one compares the structures of **3** and **4**, all the geometric parameters are within normal ranges and compare well. The only significant difference between the crystal structures is again the O6—C13—C31—C36 torsion angle, which is 4.3 (2)° in **4** and in **3**, is 24.0 (5)° for the coordinated ligand and 9.9 (5)° for the free molecule. What is interesting to note is that in both cases of the free molecule (in **3** and **4**), where the O6—C13—C31—C36 (O06—C013—C031—C036) torsion angle is significantly smaller, hydrogen-bonding interactions are observed between atoms C36(C036) and O6(O06), whereas in the case of the coordinated ligand in **3**, no hydrogen-bond interaction is observed between atoms C36 and O6, and a larger torsion angle of 24.0 (5)° is observed. The hydrogen bonding might restrain the *B* ring from twisting, which could be the reason for this observation.

The dihedral angle between the planes through C31–C36 and C21/C26/O6/C11–C13 of the ligand backbone is 5.86 (13)° for **4** and 26.17 (11) and 11.52 (10)° for the coordinated ligand and the free molecule in **3**, respectively. This correlates well with the torsion angles discussed above.

3-Hydroxyflavone, **4**, crystallized in the orthorhombic space group $P2_12_12_1$ with one molecule in the asymmetric unit and four molecules in the unit cell. A literature search revealed one other structure, with an R_{int} value of 3.6%, recorded at room temperature (Etter *et al.*, 1986). The geometric parameters are all in good correlation. Some selected bond lengths and angles are summarized in Table 2 and the molecular diagram for **4** is given in Fig. 1.

Three intermolecular (O—H···O and C—H···O) and one intramolecular (O—H···O) hydrogen-bonding interaction is observed. The hydroxy O atom (O5) forms one intramolecular and one intermolecular hydrogen-bond interaction to the carbonyl O atom (O4). These two hydrogen-bonding interactions are both three-centred interactions (bifurcated configuration; symmetry code: $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$). A π–π interaction is observed between *Cg*1 and *Cg*2 with a centroid-to-centroid distance of 3.8001 (30) Å and symmetry codes $(x+1, y, z)$ and $(x-1, y, z)$. A C—H···π interaction is also observed (C23—H23···*Cg*2), with a *Cg*···H distance of 2.9430 (8) Å. These interactions create two infinite 1D chains along the $[\bar{1}00]$ and [100] directions. When viewed along the *a* axis, the molecules pack in a head-to-head fashion in alternating 'column'-like structures, with an angle of ∼90° to the previous 'column' (in the *bc* plane). The data and an illustration of the different interactions observed in **4** are presented in Table 3 and Fig. 2. In the structure reported by Etter *et al.* (1986), the π-interactions and the total packing or potential infinite chains are not mentioned or discussed, which are both addressed herein.

3.3. ^{13}C CP/MAS NMR spectroscopy

The chemical shift values of the solid-state ^{13}C spectra provide information on the conformation of the molecules that are 'frozen' in the solid, such as any hydrogen bonding that may be present and crystal packing effects. The locked conformation of the OH group in the solid state results in an increased shielding of neighbouring C atoms, illustrated by the CP/MAS spectrum of 3-hydroxyflavone. The splitting of the C32 and C36 carbon peaks in the solid-state spectrum (130.4 and 130.2 ppm) *versus* the single peak in the liquid state for these two C atoms (127.8 ppm) indicates that these two C atoms are no longer equivalent in the solid state due to the hindered rotation of the aromatic *B* ring. A difference in chemical shift of between 0.2 and 3 ppm between the liquid- and solid-state aromatic C atoms can be attributed to the π–π and intermolecular interactions that occur when the molecules

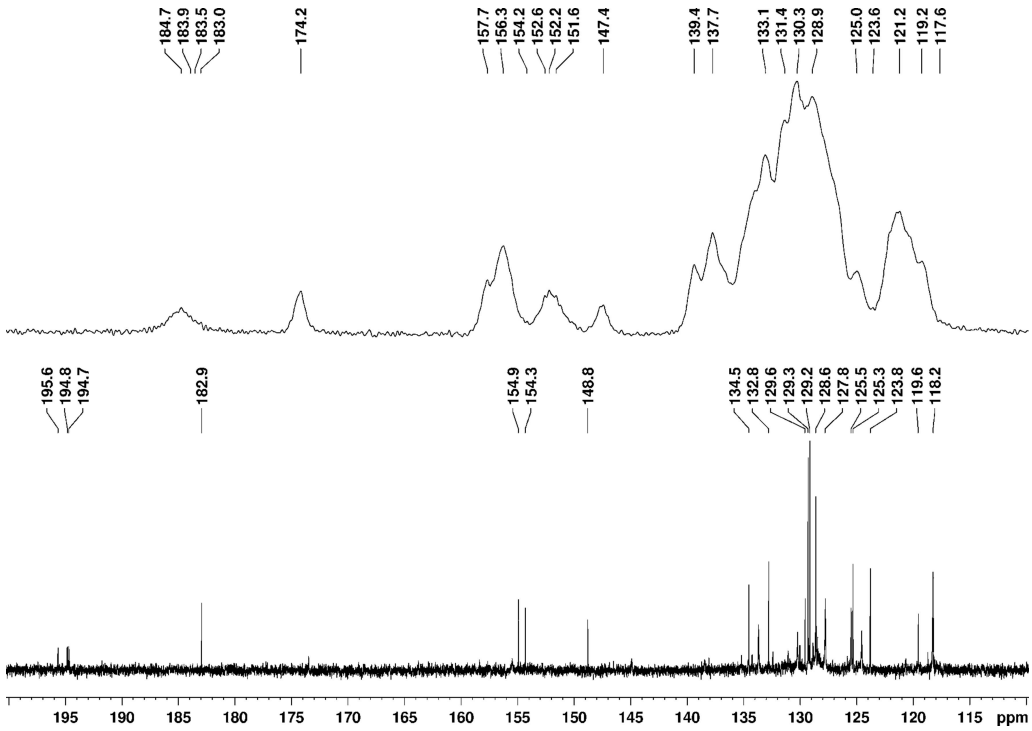


Figure 3
The liquid (bottom) and CP/MAS (top) ^{13}C spectra of **3**.

are 'frozen' in the solid. The liquid (bottom) and CP/MAS (top) ^{13}C spectra of **3** and **4** are shown in Figs. 3 and 4, respectively.

Analysis of the crystal packing of a series of flavone derivatives (Wawer & Zielinska, 2001), showed that the π–π interactions are stronger when the O6—C13—C31—C36 torsion angle is smaller. As discussed above, this torsion angle is smaller for **4** than for **3**, which would explain the smaller differences in the chemical-shift values for the aromatic C atoms in the liquid and solid state of **3**. A larger difference is however observed between the chemical-shift values of the CO groups and atom C11. This can be attributed to the

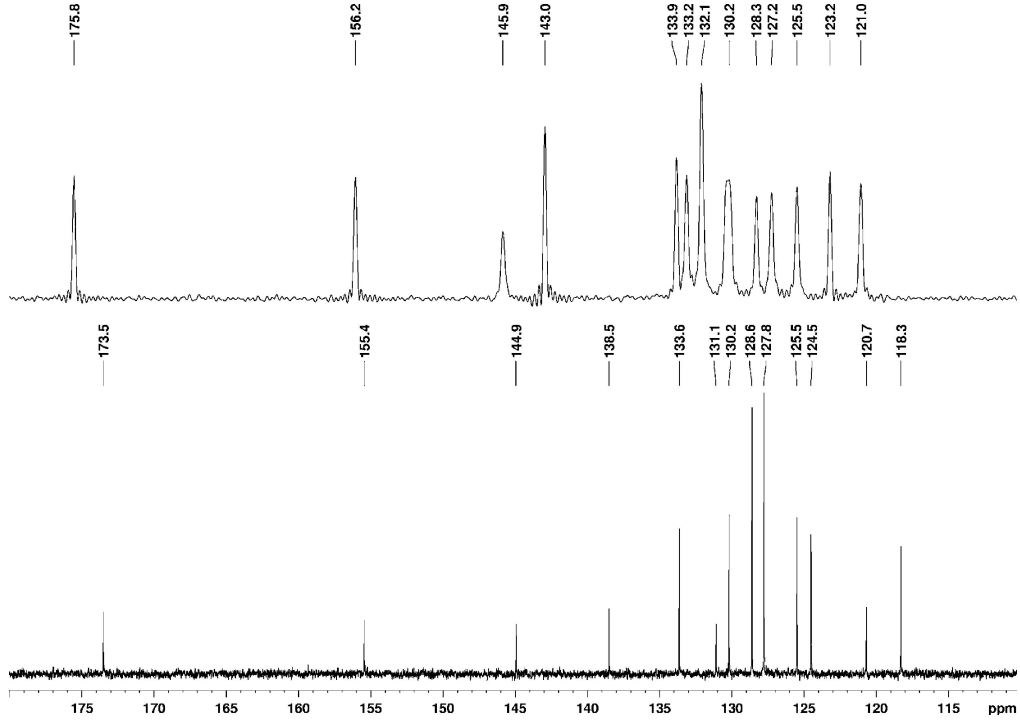


Figure 4
The liquid (bottom) and CP/MAS (top) ^{13}C spectra of **4**.

intermolecular interactions that are present in the solid-state packing. More peaks than expected are observed in the CP/MAS spectrum of **3** and can be ascribed to the free 3-hydroxyflavone molecule that cocrystallized with the Re^{I} compound in the unit cell.

4. Conclusion

This study reports some coordination-chemistry aspects of benzhydroxamic acid (BHAH) and 3-hydroxyflavone (FlavH) and Re^{I} complexes thereof, and describes some important aspects.

(i) The synthesis and crystal structures of two new Re^{I} complexes obtained by utilizing BHAH and FlavH as bidentate ligands are reported, *i.e.* tetraethylammonium *fac*-(benzhydroxamato-κ^2O,O')bromidotricarbonylrhenate(I), **1**, and *fac*-aquatricarbonyl(4-oxo-2-phenylchromen-3-olato-κ^2O,O')-rhenium(I)–3-hydroxyflavone (1/1), **3**.

(ii) The crystal structure of free 3-hydroxyflavone, **4**, was redetermined at 100 K in order to compare the packing trends and solid-state NMR spectrum with that of the solvate flavone molecule in **3**.

(iii) Molecules of **1** and **3** generate 1D chains formed through intermolecular interactions. A comparison of the coordinated 3-hydroxyflavone ligand with the uncoordinated solvate molecule and free molecule **4** shows that the last two are virtually completely planar due to hydrogen-bonding interactions compared to the first, which is able to rotate more freely.

The compounds were characterized in solution by ^{1}H and ^{13}C NMR spectroscopy and in the solid state by ^{13}C NMR spectroscopy using the cross-polarization magic angle spinning (CP/MAS) technique. The differences between the solid- and solution-state ^{13}C NMR spectra of **3** and **4** are ascribed to inter- and intramolecular interactions.

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Structures of rhenium(I) complexes with 3-hydroxyflavone and benzhydroxamic acid as *O,O′*-bidentate ligands and confirmation of π-stacking by solid-state NMR spectroscopy

Marietjie Schutte-Smith, Andreas Roodt, Roger Alberto, Linette Twigge, Hendrik Gideon Visser, Leo Kirsten and Renier Koen

Computing details

For all structures, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT-Plus* (Bruker, 2008); data reduction: *SAINT-Plus* (Bruker, 2008) and *XPREP* (Bruker, 2008); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *WinGX* (Farrugia, 2012) and *SHELXL2018* (Sheldrick, 2015); molecular graphics: *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL2018* (Sheldrick, 2015).

Tetraethylammonium *fac*-(benzhydroxamato-κ^2O,O')bromidotricarbonylrhenate(I) (7LMaSc1)

Crystal data

$(C_8H_{20}N)[ReBr(C_7H_6NO_2)(CO)_3]$
M_r = 616.52
Triclinic, $P\overline{1}$
a = 9.6321 (13) Å
b = 9.8793 (11) Å
c = 12.826 (2) Å
α = 95.806 (10)°
β = 108.520 (11)°
γ = 112.895 (7)°
V = 1030.2 (3) Å^3
Z = 2
$F(000)$ = 596
D_x = 1.987 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5976 reflections
θ = 2.5–28.3°
μ = 7.87 mm^{-1}
T = 100 K
Cuboid, colourless
0.38 × 0.25 × 0.11 mm

Data collection

CCD area detector diffractometer
Radiation source: sealed tube
phi and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.109, T_{max} = 0.421
18080 measured reflections
4957 independent reflections
4720 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 28.0°, θ_{min} = 1.7°
h = −12→12
k = −13→13
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.049
S = 1.03
4957 reflections
252 parameters
0 restraints

Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.652P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.78$ e Å^{-3}
$\Delta\rho_{min} = -1.91$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.1854 (4)	0.1312 (3)	0.1675 (2)	0.0131 (5)
C2	−0.0337 (3)	−0.1441 (3)	0.1472 (2)	0.0134 (5)
C3	−0.1219 (4)	0.0805 (3)	0.1303 (2)	0.0143 (6)
C11	0.0637 (3)	0.2422 (3)	0.4379 (2)	0.0090 (5)
C12	0.1205 (3)	0.3743 (3)	0.5326 (2)	0.0089 (5)
C13	0.1932 (3)	0.5189 (3)	0.5164 (2)	0.0112 (5)
H13	0.200584	0.529294	0.445278	0.013*
C14	0.2547 (4)	0.6473 (3)	0.6036 (2)	0.0155 (6)
H14	0.304264	0.745532	0.592324	0.019*
C15	0.2437 (3)	0.6319 (3)	0.7075 (2)	0.0158 (6)
H15	0.285682	0.719661	0.767527	0.019*
C16	0.1712 (3)	0.4878 (3)	0.7236 (2)	0.0141 (5)
H16	0.163508	0.477699	0.794685	0.017*
C17	0.1099 (3)	0.3586 (3)	0.6367 (2)	0.0108 (5)
H17	0.061047	0.260413	0.648235	0.013*
C21	0.5420 (4)	0.3084 (3)	0.6767 (2)	0.0159 (6)
H21A	0.621877	0.292673	0.650199	0.019*
H21B	0.435037	0.217975	0.636214	0.019*
C22	0.5261 (4)	0.4462 (4)	0.6438 (3)	0.0216 (7)
H22A	0.469027	0.422069	0.561092	0.032*
H22B	0.635206	0.531177	0.667625	0.032*
H22C	0.463608	0.474617	0.681341	0.032*
C23	0.4561 (3)	0.3052 (3)	0.8386 (2)	0.0132 (5)
H23A	0.357021	0.212011	0.788158	0.016*
H23B	0.433328	0.393035	0.826119	0.016*
C24	0.4852 (4)	0.2995 (4)	0.9611 (2)	0.0211 (6)
H24A	0.389219	0.291683	0.976247	0.032*
H24B	0.581410	0.392365	1.012214	0.032*
H24C	0.503936	0.210858	0.974056	0.032*
C25	0.7425 (3)	0.4676 (3)	0.8731 (2)	0.0122 (5)
H25A	0.775353	0.466013	0.954154	0.015*
H25B	0.709086	0.550202	0.865005	0.015*
C26	0.8911 (3)	0.5058 (3)	0.8422 (2)	0.0165 (6)
H26A	0.925742	0.424985	0.849587	0.025*

H26B	0.980649	0.602466	0.893561	0.025*
H26C	0.862643	0.514604	0.763558	0.025*
C27	0.6407 (3)	0.1891 (3)	0.8242 (2)	0.0143 (6)
H27A	0.725049	0.196124	0.793807	0.017*
H27B	0.689899	0.202742	0.907368	0.017*
C28	0.4989 (4)	0.0316 (3)	0.7716 (3)	0.0222 (7)
H28A	0.538413	−0.044634	0.787962	0.033*
H28B	0.449790	0.015995	0.689026	0.033*
H28C	0.416609	0.021397	0.803624	0.033*
N1	−0.0464 (3)	0.1077 (2)	0.43186 (18)	0.0093 (4)
N2	0.5959 (3)	0.3183 (2)	0.80319 (17)	0.0087 (4)
O1	0.2774 (3)	0.1839 (2)	0.12566 (18)	0.0208 (5)
O2	−0.0760 (3)	−0.2637 (2)	0.09062 (17)	0.0204 (5)
O3	−0.2210 (3)	0.0988 (2)	0.06245 (18)	0.0223 (5)
O11	0.1223 (2)	0.2589 (2)	0.36066 (15)	0.0122 (4)
O12	−0.0965 (2)	−0.0148 (2)	0.34430 (15)	0.0105 (4)
Br1	0.26528 (3)	0.01265 (3)	0.40365 (2)	0.01252 (6)
Re1	0.03945 (2)	0.05041 (2)	0.24114 (2)	0.00857 (4)
H1	−0.093 (4)	0.086 (4)	0.483 (3)	0.026 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0205 (15)	0.0112 (12)	0.0077 (11)	0.0075 (11)	0.0051 (11)	0.0023 (10)
C2	0.0164 (14)	0.0194 (14)	0.0095 (12)	0.0106 (11)	0.0070 (11)	0.0067 (11)
C3	0.0189 (15)	0.0098 (12)	0.0110 (12)	0.0029 (11)	0.0069 (11)	0.0012 (10)
C11	0.0095 (12)	0.0113 (12)	0.0074 (11)	0.0054 (10)	0.0036 (10)	0.0035 (9)
C12	0.0081 (12)	0.0095 (12)	0.0089 (11)	0.0039 (9)	0.0038 (10)	0.0000 (9)
C13	0.0102 (13)	0.0130 (12)	0.0115 (12)	0.0054 (10)	0.0052 (10)	0.0037 (10)
C14	0.0161 (14)	0.0113 (13)	0.0165 (13)	0.0044 (11)	0.0057 (11)	0.0018 (10)
C15	0.0152 (14)	0.0138 (13)	0.0145 (13)	0.0050 (11)	0.0048 (11)	−0.0024 (10)
C16	0.0125 (13)	0.0187 (14)	0.0109 (12)	0.0056 (11)	0.0066 (11)	0.0017 (10)
C17	0.0079 (12)	0.0131 (12)	0.0114 (12)	0.0040 (10)	0.0051 (10)	0.0021 (10)
C21	0.0162 (14)	0.0218 (14)	0.0055 (11)	0.0048 (11)	0.0040 (10)	0.0021 (10)
C22	0.0168 (15)	0.0314 (17)	0.0206 (15)	0.0112 (13)	0.0082 (12)	0.0174 (13)
C23	0.0087 (13)	0.0168 (13)	0.0148 (13)	0.0048 (10)	0.0068 (10)	0.0030 (10)
C24	0.0230 (16)	0.0267 (16)	0.0177 (14)	0.0091 (13)	0.0151 (13)	0.0074 (12)
C25	0.0100 (13)	0.0108 (12)	0.0094 (12)	0.0007 (10)	0.0019 (10)	−0.0010 (10)
C26	0.0107 (13)	0.0168 (14)	0.0190 (14)	0.0024 (11)	0.0067 (11)	0.0052 (11)
C27	0.0136 (14)	0.0111 (12)	0.0172 (13)	0.0057 (10)	0.0045 (11)	0.0041 (10)
C28	0.0180 (15)	0.0095 (13)	0.0385 (18)	0.0037 (11)	0.0142 (14)	0.0039 (12)
N1	0.0109 (11)	0.0095 (10)	0.0067 (10)	0.0036 (8)	0.0044 (9)	0.0002 (8)
N2	0.0081 (11)	0.0100 (10)	0.0072 (10)	0.0034 (8)	0.0032 (8)	0.0015 (8)
O1	0.0271 (12)	0.0249 (11)	0.0216 (11)	0.0143 (9)	0.0180 (10)	0.0122 (9)
O2	0.0265 (12)	0.0133 (10)	0.0167 (10)	0.0092 (9)	0.0039 (9)	−0.0012 (8)
O3	0.0241 (12)	0.0253 (11)	0.0177 (10)	0.0133 (9)	0.0044 (9)	0.0100 (9)
O11	0.0163 (10)	0.0100 (9)	0.0098 (9)	0.0039 (7)	0.0075 (8)	0.0011 (7)
O12	0.0120 (9)	0.0067 (8)	0.0086 (9)	0.0004 (7)	0.0049 (7)	−0.0022 (7)

Br1	0.01056 (13)	0.01808 (13)	0.00890 (12)	0.00574 (10)	0.00462 (10)	0.00339 (10)
Re1	0.01144 (6)	0.00867 (6)	0.00553 (6)	0.00374 (4)	0.00431 (4)	0.00140 (4)

Geometric parameters (Å, º)

C1—O1	1.159 (3)	C23—N2	1.517 (4)
C1—Re1	1.905 (3)	C23—C24	1.518 (4)
C2—O2	1.163 (3)	C23—H23A	0.9900
C2—Re1	1.892 (3)	C23—H23B	0.9900
C3—O3	1.157 (3)	C24—H24A	0.9800
C3—Re1	1.889 (3)	C24—H24B	0.9800
C11—O11	1.282 (3)	C24—H24C	0.9800
C11—N1	1.314 (3)	C25—N2	1.510 (3)
C11—C12	1.476 (4)	C25—C26	1.523 (4)
C12—C17	1.391 (3)	C25—H25A	0.9900
C12—C13	1.396 (3)	C25—H25B	0.9900
C13—C14	1.384 (4)	C26—H26A	0.9800
C13—H13	0.9500	C26—H26B	0.9800
C14—C15	1.389 (4)	C26—H26C	0.9800
C14—H14	0.9500	C27—C28	1.513 (4)
C15—C16	1.390 (4)	C27—N2	1.521 (3)
C15—H15	0.9500	C27—H27A	0.9900
C16—C17	1.388 (4)	C27—H27B	0.9900
C16—H16	0.9500	C28—H28A	0.9800
C17—H17	0.9500	C28—H28B	0.9800
C21—C22	1.515 (4)	C28—H28C	0.9800
C21—N2	1.518 (3)	N1—O12	1.373 (3)
C21—H21A	0.9900	N1—H1	0.91 (4)
C21—H21B	0.9900	O11—Re1	2.1292 (19)
C22—H22A	0.9800	O12—Re1	2.1204 (19)
C22—H22B	0.9800	Br1—Re1	2.6690 (5)
C22—H22C	0.9800		

O1—C1—Re1	177.9 (2)	N2—C25—H25A	108.4
O2—C2—Re1	178.7 (3)	C26—C25—H25A	108.4
O3—C3—Re1	179.9 (3)	N2—C25—H25B	108.4
O11—C11—N1	119.6 (2)	C26—C25—H25B	108.4
O11—C11—C12	119.6 (2)	H25A—C25—H25B	107.5
N1—C11—C12	120.8 (2)	C25—C26—H26A	109.5
C17—C12—C13	120.0 (2)	C25—C26—H26B	109.5
C17—C12—C11	122.3 (2)	H26A—C26—H26B	109.5
C13—C12—C11	117.6 (2)	C25—C26—H26C	109.5
C14—C13—C12	120.3 (2)	H26A—C26—H26C	109.5
C14—C13—H13	119.8	H26B—C26—H26C	109.5
C12—C13—H13	119.8	C28—C27—N2	114.7 (2)
C13—C14—C15	119.8 (2)	C28—C27—H27A	108.6
C13—C14—H14	120.1	N2—C27—H27A	108.6
C15—C14—H14	120.1	C28—C27—H27B	108.6

C14—C15—C16	119.9 (3)	N2—C27—H27B	108.6
C14—C15—H15	120.0	H27A—C27—H27B	107.6
C16—C15—H15	120.0	C27—C28—H28A	109.5
C17—C16—C15	120.6 (3)	C27—C28—H28B	109.5
C17—C16—H16	119.7	H28A—C28—H28B	109.5
C15—C16—H16	119.7	C27—C28—H28C	109.5
C16—C17—C12	119.4 (2)	H28A—C28—H28C	109.5
C16—C17—H17	120.3	H28B—C28—H28C	109.5
C12—C17—H17	120.3	C11—N1—O12	120.2 (2)
C22—C21—N2	115.0 (2)	C11—N1—H1	125 (2)
C22—C21—H21A	108.5	O12—N1—H1	114 (2)
N2—C21—H21A	108.5	C25—N2—C23	108.3 (2)
C22—C21—H21B	108.5	C25—N2—C21	111.85 (19)
N2—C21—H21B	108.5	C23—N2—C21	108.7 (2)
H21A—C21—H21B	107.5	C25—N2—C27	109.0 (2)
C21—C22—H22A	109.5	C23—N2—C27	111.0 (2)
C21—C22—H22B	109.5	C21—N2—C27	108.1 (2)
H22A—C22—H22B	109.5	C11—O11—Re1	113.20 (16)
C21—C22—H22C	109.5	N1—O12—Re1	109.83 (14)
H22A—C22—H22C	109.5	C3—Re1—C2	89.93 (12)
H22B—C22—H22C	109.5	C3—Re1—C1	89.58 (12)
N2—C23—C24	115.2 (2)	C2—Re1—C1	88.02 (12)
N2—C23—H23A	108.5	C3—Re1—O12	94.96 (10)
C24—C23—H23A	108.5	C2—Re1—O12	98.84 (10)
N2—C23—H23B	108.5	C1—Re1—O12	171.76 (9)
C24—C23—H23B	108.5	C3—Re1—O11	94.10 (10)
H23A—C23—H23B	107.5	C2—Re1—O11	174.27 (8)
C23—C24—H24A	109.5	C1—Re1—O11	96.07 (9)
C23—C24—H24B	109.5	O12—Re1—O11	76.78 (7)
H24A—C24—H24B	109.5	C3—Re1—Br1	177.92 (9)
C23—C24—H24C	109.5	C2—Re1—Br1	91.65 (8)
H24A—C24—H24C	109.5	C1—Re1—Br1	91.82 (8)
H24B—C24—H24C	109.5	O12—Re1—Br1	83.47 (5)
N2—C25—C26	115.5 (2)	O11—Re1—Br1	84.23 (5)

O11—C11—C12—C17	−156.9 (3)	C26—C25—N2—C21	−55.6 (3)
N1—C11—C12—C17	23.2 (4)	C26—C25—N2—C27	63.9 (3)
O11—C11—C12—C13	20.4 (4)	C24—C23—N2—C25	−63.3 (3)
N1—C11—C12—C13	−159.5 (2)	C24—C23—N2—C21	175.0 (2)
C17—C12—C13—C14	−0.1 (4)	C24—C23—N2—C27	56.3 (3)
C11—C12—C13—C14	−177.5 (3)	C22—C21—N2—C25	−48.1 (3)
C12—C13—C14—C15	−0.1 (4)	C22—C21—N2—C23	71.4 (3)
C13—C14—C15—C16	0.0 (4)	C22—C21—N2—C27	−168.1 (2)
C14—C15—C16—C17	0.2 (4)	C28—C27—N2—C25	172.4 (2)
C15—C16—C17—C12	−0.4 (4)	C28—C27—N2—C23	53.3 (3)
C13—C12—C17—C16	0.4 (4)	C28—C27—N2—C21	−65.8 (3)
C11—C12—C17—C16	177.6 (3)	N1—C11—O11—Re1	−5.3 (3)
O11—C11—N1—O12	1.1 (4)	C12—C11—O11—Re1	174.80 (18)

C12—C11—N1—O12	−179.0 (2)	C11—N1—O12—Re1	3.7 (3)
C26—C25—N2—C23	−175.3 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br1^{i}	0.91 (4)	2.52 (4)	3.420 (2)	170 (3)
C23—H23*A*···O12^{i}	0.99	2.41	3.388 (3)	170
C25—H25*B*···O1^{ii}	0.99	2.57	3.520 (4)	162
C26—H26*A*···O2^{iii}	0.98	2.56	3.520 (4)	166
C27—H27*B*···O3^{iv}	0.99	2.40	3.286 (3)	149
C17—H17···O12^{i}	0.95	2.59	3.385 (3)	142
C25—H25*A*···O2^{v}	0.99	2.59	3.111 (3)	113

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*, −*z*+1; (iv) *x*+1, *y*, *z*+1; (v) *x*+1, *y*+1, *z*+1.

fac-Aquatricarbonyl(4-oxo-2-phenylchromen-3-olato-\ κ^2O,O')rhenium(I)–3-hydroxyflavone (1/1) (10Amsc4)

Crystal data

$[Re(C_{15}H_9O_3)(CO)_3(H_2O)]\cdot C_{15}H_{10}O_3$
M_r = 763.70
Triclinic, $P\overline{1}$
a = 10.5209 (15) Å
b = 11.9365 (17) Å
c = 12.4455 (17) Å
α = 108.277 (7)°
β = 102.745 (7)°
γ = 104.252 (7)°
V = 1361.0 (3) Å^3
Z = 2
$F(000)$ = 748
D_x = 1.864 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 9860 reflections
θ = 2.9–28.6°
μ = 4.53 mm^{-1}
T = 100 K
Cuboid, yellow
0.55 × 0.17 × 0.08 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.417, T_{max} = 0.699
23222 measured reflections
6700 independent reflections
6045 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 28.6°, θ_{min} = 3.5°
h = −14→14
k = −16→16
l = −16→16

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.060
S = 1.06
6700 reflections
406 parameters
0 restraints
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0156P)^2 + 3.4093P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.40 e Å^{-3}
$\Delta\rho_{min}$ = −2.10 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5140 (4)	−0.2364 (3)	0.4055 (3)	0.0199 (7)
C2	0.3810 (4)	−0.2744 (3)	0.1859 (3)	0.0204 (7)
C3	0.6494 (4)	−0.2215 (3)	0.2549 (3)	0.0196 (7)
C11	0.6247 (4)	0.0961 (3)	0.2846 (3)	0.0198 (7)
C011	0.2049 (3)	−0.0071 (3)	1.1005 (3)	0.0202 (7)
C012	0.1389 (3)	−0.0859 (3)	0.9754 (3)	0.0192 (7)
C12	0.6965 (4)	0.1271 (3)	0.4072 (3)	0.0190 (7)
C013	0.1113 (3)	−0.0380 (3)	0.8907 (3)	0.0175 (7)
C13	0.7720 (4)	0.2509 (3)	0.4809 (3)	0.0189 (7)
C21	0.7148 (4)	0.3169 (3)	0.3205 (3)	0.0209 (7)
C021	0.2151 (3)	0.1691 (3)	1.0409 (3)	0.0189 (7)
C22	0.7313 (4)	0.4166 (3)	0.2842 (3)	0.0239 (8)
H22	0.787106	0.499269	0.339470	0.029*
C022	0.2528 (4)	0.2964 (3)	1.0638 (3)	0.0229 (7)
H022	0.232380	0.324554	1.000692	0.027*
C23	0.6658 (4)	0.3942 (4)	0.1671 (3)	0.0255 (8)
H23	0.676381	0.461921	0.141326	0.031*
C023	0.3209 (4)	0.3812 (4)	1.1806 (3)	0.0252 (8)
H023	0.347574	0.468651	1.198032	0.030*
C24	0.5831 (4)	0.2715 (4)	0.0852 (3)	0.0227 (7)
H24	0.537225	0.256493	0.004552	0.027*
C024	0.3510 (4)	0.3394 (4)	1.2738 (3)	0.0261 (8)
H024	0.397856	0.398781	1.353607	0.031*
C025	0.3136 (4)	0.2146 (4)	1.2504 (3)	0.0230 (8)
H025	0.333851	0.186976	1.313909	0.028*
C25	0.5693 (4)	0.1744 (3)	0.1224 (3)	0.0195 (7)
H25	0.513423	0.091696	0.067187	0.023*
C026	0.2446 (3)	0.1261 (3)	1.1318 (3)	0.0187 (7)
C26	0.6363 (4)	0.1949 (3)	0.2411 (3)	0.0194 (7)
C31	0.8486 (3)	0.3033 (3)	0.6094 (3)	0.0186 (7)
C031	0.0386 (3)	−0.1072 (3)	0.7614 (3)	0.0184 (7)
C32	0.9040 (4)	0.2321 (3)	0.6644 (3)	0.0211 (7)
H32	0.887587	0.146275	0.619442	0.025*
C032	0.0070 (4)	−0.2361 (3)	0.7066 (3)	0.0225 (7)
H032	0.036121	−0.281227	0.752195	0.027*
C033	−0.0667 (4)	−0.2990 (4)	0.5857 (3)	0.0267 (8)
H033	−0.086890	−0.386934	0.549063	0.032*
C33	0.9827 (4)	0.2869 (3)	0.7842 (3)	0.0220 (7)
H33	1.020553	0.238159	0.820573	0.026*

C034	−0.1115 (4)	−0.2356 (4)	0.5174 (3)	0.0242 (8)
H034	−0.164075	−0.279874	0.435007	0.029*
C34	1.0072 (4)	0.4102 (4)	0.8516 (3)	0.0231 (7)
H34	1.063253	0.447020	0.933291	0.028*
C35	0.9494 (4)	0.4802 (3)	0.7994 (3)	0.0238 (8)
H35	0.963214	0.564889	0.846217	0.029*
C035	−0.0788 (4)	−0.1076 (4)	0.5705 (3)	0.0272 (8)
H035	−0.108130	−0.063143	0.524232	0.033*
C36	0.8714 (4)	0.4280 (3)	0.6793 (3)	0.0211 (7)
H36	0.833146	0.477405	0.644207	0.025*
C036	−0.0031 (4)	−0.0433 (3)	0.6912 (3)	0.0249 (8)
H036	0.020503	0.045221	0.726428	0.030*
O1	0.5028 (3)	−0.2981 (3)	0.4610 (2)	0.0277 (6)
O2	0.2923 (3)	−0.3565 (3)	0.1074 (2)	0.0297 (6)
O3	0.7187 (3)	−0.2755 (3)	0.2184 (2)	0.0305 (6)
O04	0.2208 (3)	−0.0595 (2)	1.1723 (2)	0.0242 (5)
O4	0.5511 (3)	−0.0166 (2)	0.2184 (2)	0.0210 (5)
O5	0.6847 (2)	0.0325 (2)	0.4444 (2)	0.0191 (5)
O05	0.1030 (3)	−0.2108 (2)	0.9494 (2)	0.0250 (6)
H05	0.132731	−0.222694	1.011772	0.038*
O6	0.7796 (2)	0.3434 (2)	0.4386 (2)	0.0200 (5)
O06	0.1490 (2)	0.0888 (2)	0.9236 (2)	0.0191 (5)
O7	0.4034 (3)	−0.0289 (2)	0.3719 (3)	0.0209 (6)
Re1	0.53064 (2)	−0.13900 (2)	0.31117 (2)	0.01536 (4)
H7A	0.354 (5)	−0.031 (4)	0.329 (4)	0.021 (13)*
H7B	0.369 (5)	−0.047 (5)	0.425 (5)	0.045 (15)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0201 (17)	0.0165 (17)	0.0177 (16)	0.0051 (14)	0.0020 (14)	0.0035 (14)
C2	0.0226 (17)	0.0241 (19)	0.0163 (16)	0.0082 (15)	0.0088 (14)	0.0082 (15)
C3	0.0207 (17)	0.0171 (17)	0.0152 (16)	0.0029 (14)	0.0020 (13)	0.0042 (13)
C11	0.0214 (17)	0.0195 (18)	0.0183 (16)	0.0087 (14)	0.0062 (14)	0.0059 (14)
C011	0.0151 (15)	0.0267 (19)	0.0200 (17)	0.0096 (14)	0.0048 (13)	0.0093 (15)
C012	0.0150 (15)	0.0181 (17)	0.0227 (17)	0.0053 (13)	0.0035 (13)	0.0079 (14)
C12	0.0196 (16)	0.0160 (17)	0.0209 (17)	0.0071 (14)	0.0071 (14)	0.0052 (14)
C013	0.0144 (15)	0.0161 (16)	0.0205 (16)	0.0058 (13)	0.0037 (13)	0.0061 (14)
C13	0.0195 (16)	0.0185 (17)	0.0190 (16)	0.0065 (14)	0.0056 (14)	0.0083 (14)
C21	0.0230 (17)	0.0227 (19)	0.0166 (16)	0.0097 (15)	0.0053 (14)	0.0065 (14)
C021	0.0153 (15)	0.0223 (18)	0.0162 (16)	0.0079 (14)	0.0024 (13)	0.0046 (14)
C22	0.0291 (19)	0.0166 (18)	0.0224 (18)	0.0058 (15)	0.0042 (15)	0.0073 (15)
C022	0.0229 (17)	0.0210 (18)	0.0214 (17)	0.0101 (15)	0.0020 (14)	0.0056 (15)
C23	0.0298 (19)	0.024 (2)	0.0246 (19)	0.0094 (16)	0.0070 (16)	0.0137 (16)
C023	0.0240 (18)	0.0202 (19)	0.0258 (19)	0.0077 (15)	0.0037 (15)	0.0048 (15)
C24	0.0245 (18)	0.029 (2)	0.0170 (17)	0.0115 (16)	0.0072 (14)	0.0105 (15)
C024	0.0242 (18)	0.026 (2)	0.0190 (17)	0.0084 (16)	0.0004 (15)	0.0012 (15)
C025	0.0188 (17)	0.029 (2)	0.0176 (17)	0.0073 (15)	0.0026 (14)	0.0080 (15)

C25	0.0203 (16)	0.0205 (18)	0.0170 (16)	0.0080 (14)	0.0050 (14)	0.0061 (14)
C026	0.0136 (15)	0.0217 (18)	0.0192 (16)	0.0067 (13)	0.0037 (13)	0.0066 (14)
C26	0.0189 (16)	0.0214 (18)	0.0184 (16)	0.0073 (14)	0.0063 (14)	0.0081 (14)
C31	0.0165 (16)	0.0184 (17)	0.0166 (16)	0.0040 (13)	0.0029 (13)	0.0045 (14)
C031	0.0163 (15)	0.0216 (18)	0.0185 (16)	0.0083 (14)	0.0047 (13)	0.0088 (14)
C32	0.0205 (17)	0.0176 (18)	0.0196 (17)	0.0078 (14)	0.0012 (14)	0.0027 (14)
C032	0.0256 (18)	0.0202 (18)	0.0219 (18)	0.0081 (15)	0.0056 (15)	0.0095 (15)
C033	0.036 (2)	0.0195 (19)	0.0204 (18)	0.0080 (16)	0.0051 (16)	0.0064 (15)
C33	0.0193 (17)	0.0253 (19)	0.0186 (17)	0.0075 (15)	0.0017 (14)	0.0081 (15)
C034	0.0283 (19)	0.0232 (19)	0.0157 (16)	0.0066 (15)	0.0026 (15)	0.0052 (14)
C34	0.0191 (17)	0.028 (2)	0.0192 (17)	0.0053 (15)	0.0049 (14)	0.0077 (15)
C35	0.0284 (19)	0.0151 (17)	0.0214 (18)	0.0009 (15)	0.0058 (15)	0.0053 (14)
C035	0.037 (2)	0.026 (2)	0.0187 (17)	0.0150 (17)	0.0029 (16)	0.0100 (16)
C36	0.0264 (18)	0.0156 (17)	0.0191 (17)	0.0072 (14)	0.0046 (14)	0.0057 (14)
C036	0.032 (2)	0.0180 (18)	0.0221 (18)	0.0109 (16)	0.0043 (16)	0.0064 (15)
O1	0.0321 (14)	0.0296 (15)	0.0262 (14)	0.0114 (12)	0.0075 (12)	0.0176 (12)
O2	0.0269 (14)	0.0269 (15)	0.0207 (13)	−0.0043 (12)	0.0038 (11)	0.0039 (12)
O3	0.0307 (14)	0.0344 (16)	0.0299 (15)	0.0169 (13)	0.0121 (12)	0.0107 (13)
O04	0.0247 (13)	0.0261 (14)	0.0215 (13)	0.0077 (11)	0.0019 (11)	0.0134 (11)
O4	0.0252 (13)	0.0185 (13)	0.0187 (12)	0.0080 (10)	0.0052 (10)	0.0072 (10)
O5	0.0207 (12)	0.0169 (12)	0.0150 (11)	0.0052 (10)	0.0016 (10)	0.0041 (10)
O05	0.0311 (14)	0.0188 (13)	0.0213 (13)	0.0075 (11)	0.0003 (11)	0.0093 (11)
O6	0.0238 (12)	0.0134 (12)	0.0175 (12)	0.0034 (10)	0.0008 (10)	0.0054 (10)
O06	0.0202 (12)	0.0164 (12)	0.0169 (11)	0.0067 (10)	0.0006 (10)	0.0049 (10)
O7	0.0211 (13)	0.0229 (14)	0.0177 (13)	0.0105 (11)	0.0016 (12)	0.0079 (11)
Re1	0.01730 (7)	0.01368 (7)	0.01221 (7)	0.00484 (5)	0.00184 (5)	0.00370 (5)

Geometric parameters (Å, º)

C1—O1	1.160 (4)	C24—H24	0.9500
C1—Re1	1.900 (4)	C024—C025	1.360 (5)
C2—O2	1.154 (4)	C024—H024	0.9500
C2—Re1	1.899 (4)	C025—C026	1.412 (5)
C3—O3	1.161 (4)	C025—H025	0.9500
C3—Re1	1.892 (4)	C25—C26	1.403 (5)
C11—O4	1.265 (4)	C25—H25	0.9500
C11—C12	1.426 (5)	C31—C36	1.397 (5)
C11—C26	1.433 (5)	C31—C32	1.400 (5)
C011—O04	1.246 (4)	C031—C032	1.390 (5)
C011—C026	1.438 (5)	C031—C036	1.398 (5)
C011—C012	1.441 (5)	C32—C33	1.384 (5)
C012—O05	1.354 (4)	C32—H32	0.9500
C012—C013	1.359 (5)	C032—C033	1.385 (5)
C12—O5	1.338 (4)	C032—H032	0.9500
C12—C13	1.380 (5)	C033—C034	1.385 (5)
C013—O06	1.364 (4)	C033—H033	0.9500
C013—C031	1.473 (5)	C33—C34	1.370 (5)
C13—O6	1.357 (4)	C33—H33	0.9500

C13—C31	1.468 (5)	C034—C035	1.377 (5)
C21—O6	1.373 (4)	C034—H034	0.9500
C21—C22	1.385 (5)	C34—C35	1.381 (5)
C21—C26	1.388 (5)	C34—H34	0.9500
C021—O06	1.371 (4)	C35—C36	1.385 (5)
C021—C022	1.389 (5)	C35—H35	0.9500
C021—C026	1.389 (5)	C035—C036	1.388 (5)
C22—C23	1.376 (5)	C035—H035	0.9500
C22—H22	0.9500	C36—H36	0.9500
C022—C023	1.383 (5)	C036—H036	0.9500
C022—H022	0.9500	O4—Re1	2.128 (2)
C23—C24	1.410 (5)	O5—Re1	2.149 (2)
C23—H23	0.9500	O05—H05	0.8400
C023—C024	1.404 (5)	O7—Re1	2.187 (3)
C023—H023	0.9500	O7—H7A	0.65 (4)
C24—C25	1.366 (5)	O7—H7B	0.87 (5)

O1—C1—Re1	178.6 (3)	C36—C31—C13	120.0 (3)
O2—C2—Re1	177.9 (3)	C32—C31—C13	121.6 (3)
O3—C3—Re1	177.9 (3)	C032—C031—C036	118.4 (3)
O4—C11—C12	119.3 (3)	C032—C031—C013	121.8 (3)
O4—C11—C26	122.1 (3)	C036—C031—C013	119.7 (3)
C12—C11—C26	118.6 (3)	C33—C32—C31	119.9 (3)
O04—C011—C026	125.6 (3)	C33—C32—H32	120.1
O04—C011—C012	117.7 (3)	C31—C32—H32	120.1
C026—C011—C012	116.7 (3)	C033—C032—C031	120.2 (3)
O05—C012—C013	122.8 (3)	C033—C032—H032	119.9
O05—C012—C011	115.0 (3)	C031—C032—H032	119.9
C013—C012—C011	122.2 (3)	C032—C033—C034	121.0 (3)
O5—C12—C13	123.6 (3)	C032—C033—H033	119.5
O5—C12—C11	117.0 (3)	C034—C033—H033	119.5
C13—C12—C11	119.4 (3)	C34—C33—C32	121.4 (3)
C012—C013—O06	119.6 (3)	C34—C33—H33	119.3
C012—C013—C031	127.9 (3)	C32—C33—H33	119.3
O06—C013—C031	112.5 (3)	C035—C034—C033	119.1 (3)
O6—C13—C12	121.1 (3)	C035—C034—H034	120.4
O6—C13—C31	110.7 (3)	C033—C034—H034	120.4
C12—C13—C31	128.1 (3)	C33—C34—C35	119.3 (3)
O6—C21—C22	117.4 (3)	C33—C34—H34	120.4
O6—C21—C26	121.0 (3)	C35—C34—H34	120.4
C22—C21—C26	121.6 (3)	C34—C35—C36	120.5 (3)
O06—C021—C022	116.3 (3)	C34—C35—H35	119.8
O06—C021—C026	122.1 (3)	C36—C35—H35	119.8
C022—C021—C026	121.6 (3)	C034—C035—C036	120.4 (3)
C23—C22—C21	119.1 (3)	C034—C035—H035	119.8
C23—C22—H22	120.4	C036—C035—H035	119.8
C21—C22—H22	120.4	C35—C36—C31	120.6 (3)
C023—C022—C021	118.4 (3)	C35—C36—H36	119.7

C023—C022—H022	120.8	C31—C36—H36	119.7
C021—C022—H022	120.8	C035—C036—C031	120.8 (3)
C22—C23—C24	120.4 (3)	C035—C036—H036	119.6
C22—C23—H23	119.8	C031—C036—H036	119.6
C24—C23—H23	119.8	C11—O4—Re1	114.1 (2)
C022—C023—C024	120.7 (4)	C12—O5—Re1	111.7 (2)
C022—C023—H023	119.6	C012—O05—H05	109.5
C024—C023—H023	119.6	C13—O6—C21	121.2 (3)
C25—C24—C23	119.6 (3)	C013—O06—C021	121.1 (3)
C25—C24—H24	120.2	Re1—O7—H7A	114 (4)
C23—C24—H24	120.2	Re1—O7—H7B	114 (3)
C025—C024—C023	120.4 (3)	H7A—O7—H7B	110 (5)
C025—C024—H024	119.8	C3—Re1—C2	87.10 (15)
C023—C024—H024	119.8	C3—Re1—C1	87.17 (15)
C024—C025—C026	120.0 (3)	C2—Re1—C1	87.16 (15)
C024—C025—H025	120.0	C3—Re1—O4	96.33 (13)
C026—C025—H025	120.0	C2—Re1—O4	96.34 (12)
C24—C25—C26	121.0 (3)	C1—Re1—O4	175.16 (12)
C24—C25—H25	119.5	C3—Re1—O5	98.98 (12)
C26—C25—H25	119.5	C2—Re1—O5	171.17 (12)
C021—C026—C025	118.8 (3)	C1—Re1—O5	99.46 (12)
C021—C026—C011	118.3 (3)	O4—Re1—O5	76.72 (9)
C025—C026—C011	122.9 (3)	C3—Re1—O7	174.51 (13)
C21—C26—C25	118.3 (3)	C2—Re1—O7	95.38 (13)
C21—C26—C11	118.7 (3)	C1—Re1—O7	97.83 (13)
C25—C26—C11	123.0 (3)	O4—Re1—O7	78.55 (10)
C36—C31—C32	118.4 (3)	O5—Re1—O7	78.02 (10)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O7—H7*A*···O04^{i}	0.65 (4)	2.00 (5)	2.641 (4)	167 (5)
O7—H7*B*···O5^{ii}	0.87 (5)	1.81 (6)	2.658 (4)	162 (5)
O05—H05···O04	0.84	2.12	2.595 (4)	115
C036—H036···O06	0.95	2.35	2.696 (4)	101
C032—H032···O05	0.95	2.21	2.859 (4)	125
C32—H32···O5	0.95	2.41	2.985 (4)	119
C35—H35···O05^{iii}	0.95	2.46	3.334 (4)	153

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) −*x*+1, −*y*, −*z*+1; (iii) *x*+1, *y*+1, *z*.

2-Phenylchromen-4-one (10RMSc3)

Crystal data

$C_{15}H_{10}O_3$
M_r = 238.23
Orthorhombic, $P2_12_12_1$
a = 5.3502 (6) Å
b = 11.3531 (14) Å
c = 18.063 (2) Å
V = 1097.2 (2) Å^3
Z = 4
F(000) = 496
D_x = 1.442 Mg m^{-3}

Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 6732 reflections
θ = 2.9–28.2°
μ = 0.10 mm^{-1}

T = 100 K
Cuboid, colourless
0.37 × 0.17 × 0.15 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2008)
T_{min} = 0.980, T_{max} = 0.985
17120 measured reflections

2621 independent reflections
2376 reflections with $I > 2\sigma(I)$
R_{int} = 0.033
θ_{max} = 28.0°, θ_{min} = 3.8°
h = −7→7
k = −14→14
l = −23→23

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
S = 1.07
2621 reflections
165 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0394P)^2 + 0.260P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Refined as an inversion twin
Absolute structure parameter: −0.5 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
C11	0.1494 (3)	0.89389 (16)	0.55141 (10)	0.0162 (4)
C12	−0.0276 (3)	0.89383 (16)	0.61248 (10)	0.0163 (4)
C13	−0.0335 (3)	0.98193 (15)	0.66332 (10)	0.0164 (4)
C21	0.3073 (3)	1.07756 (16)	0.60398 (10)	0.0174 (4)
C22	0.4691 (4)	1.17374 (17)	0.60567 (11)	0.0203 (4)
H22	0.452871	1.232550	0.642778	0.024*
C23	0.6529 (4)	1.18193 (17)	0.55248 (11)	0.0222 (4)
H23	0.763964	1.247233	0.552763	0.027*
C24	0.6776 (4)	1.09508 (17)	0.49812 (11)	0.0215 (4)
H24	0.805645	1.101408	0.461886	0.026*
C25	0.5170 (3)	1.00045 (17)	0.49696 (10)	0.0189 (4)
H25	0.534973	0.941415	0.460064	0.023*
C26	0.3258 (3)	0.99081 (16)	0.55035 (10)	0.0172 (4)
C31	−0.2061 (3)	0.99745 (17)	0.72618 (10)	0.0176 (4)
C32	−0.4076 (4)	0.92170 (17)	0.73825 (10)	0.0192 (4)

H32	−0.430858	0.855244	0.707050	0.023*
C33	−0.5745 (4)	0.94314 (18)	0.79582 (11)	0.0215 (4)
H33	−0.712023	0.891625	0.803382	0.026*
C34	−0.5413 (4)	1.03891 (18)	0.84203 (11)	0.0225 (4)
H34	−0.657024	1.053599	0.880846	0.027*
C35	−0.3390 (4)	1.11355 (18)	0.83171 (11)	0.0237 (4)
H35	−0.314463	1.178438	0.864116	0.028*
C36	−0.1722 (4)	1.09365 (17)	0.77409 (10)	0.0203 (4)
H36	−0.034600	1.145332	0.767048	0.024*
O4	0.1397 (2)	0.81458 (11)	0.50448 (7)	0.0202 (3)
O5	−0.1881 (3)	0.80217 (12)	0.61550 (7)	0.0204 (3)
H5	−0.193023	0.768617	0.574078	0.031*
O6	0.1319 (2)	1.07378 (11)	0.65851 (7)	0.0182 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.0176 (9)	0.0150 (9)	0.0159 (9)	0.0034 (7)	−0.0022 (7)	0.0001 (7)
C12	0.0180 (9)	0.0148 (9)	0.0161 (9)	−0.0008 (7)	−0.0027 (7)	0.0017 (7)
C13	0.0183 (8)	0.0137 (9)	0.0170 (9)	0.0003 (7)	−0.0019 (7)	0.0015 (7)
C21	0.0184 (9)	0.0161 (9)	0.0176 (9)	0.0014 (7)	−0.0014 (7)	0.0033 (8)
C22	0.0223 (10)	0.0151 (9)	0.0234 (10)	−0.0005 (7)	−0.0035 (8)	0.0004 (8)
C23	0.0208 (9)	0.0183 (9)	0.0274 (10)	−0.0022 (8)	−0.0020 (8)	0.0050 (8)
C24	0.0181 (9)	0.0237 (10)	0.0227 (10)	0.0013 (8)	0.0008 (8)	0.0044 (8)
C25	0.0195 (9)	0.0183 (9)	0.0189 (9)	0.0037 (8)	0.0000 (7)	0.0009 (8)
C26	0.0184 (9)	0.0157 (9)	0.0175 (9)	0.0024 (7)	−0.0023 (7)	0.0021 (7)
C31	0.0199 (8)	0.0165 (9)	0.0163 (9)	0.0046 (7)	−0.0018 (7)	0.0013 (7)
C32	0.0220 (9)	0.0167 (9)	0.0188 (9)	0.0017 (7)	−0.0023 (7)	0.0009 (8)
C33	0.0221 (10)	0.0209 (10)	0.0217 (10)	0.0032 (8)	0.0005 (7)	0.0033 (8)
C34	0.0248 (9)	0.0245 (10)	0.0184 (9)	0.0088 (8)	0.0024 (7)	0.0009 (8)
C35	0.0280 (10)	0.0232 (10)	0.0198 (10)	0.0063 (8)	−0.0022 (8)	−0.0045 (8)
C36	0.0226 (9)	0.0184 (10)	0.0198 (10)	0.0005 (7)	−0.0026 (7)	−0.0007 (7)
O4	0.0233 (7)	0.0181 (7)	0.0190 (7)	0.0000 (5)	0.0006 (5)	−0.0044 (5)
O5	0.0245 (7)	0.0181 (7)	0.0187 (7)	−0.0053 (6)	0.0025 (5)	−0.0046 (5)
O6	0.0218 (6)	0.0146 (6)	0.0184 (7)	−0.0027 (5)	0.0010 (5)	−0.0028 (5)

Geometric parameters (Å, º)

C11—O4	1.238 (2)	C24—H24	0.9500
C11—C26	1.450 (3)	C25—C26	1.410 (3)
C11—C12	1.454 (2)	C25—H25	0.9500
C12—O5	1.350 (2)	C31—C32	1.396 (3)
C12—C13	1.358 (2)	C31—C36	1.405 (3)
C13—O6	1.370 (2)	C32—C33	1.392 (3)
C13—C31	1.474 (2)	C32—H32	0.9500
C21—O6	1.361 (2)	C33—C34	1.382 (3)
C21—C26	1.385 (3)	C33—H33	0.9500
C21—C22	1.394 (3)	C34—C35	1.387 (3)

C22—C23	1.378 (3)	C34—H34	0.9500
C22—H22	0.9500	C35—C36	1.390 (3)
C23—C24	1.398 (3)	C35—H35	0.9500
C23—H23	0.9500	C36—H36	0.9500
C24—C25	1.376 (3)	O5—H5	0.8400

O4—C11—C26	124.77 (16)	C21—C26—C25	118.36 (17)
O4—C11—C12	119.48 (17)	C21—C26—C11	118.94 (16)
C26—C11—C12	115.75 (15)	C25—C26—C11	122.69 (16)
O5—C12—C13	121.70 (16)	C32—C31—C36	118.82 (17)
O5—C12—C11	116.44 (16)	C32—C31—C13	122.02 (16)
C13—C12—C11	121.85 (17)	C36—C31—C13	119.12 (17)
C12—C13—O6	120.17 (16)	C33—C32—C31	120.28 (18)
C12—C13—C31	128.57 (16)	C33—C32—H32	119.9
O6—C13—C31	111.24 (14)	C31—C32—H32	119.9
O6—C21—C26	122.21 (16)	C34—C33—C32	120.43 (19)
O6—C21—C22	115.91 (16)	C34—C33—H33	119.8
C26—C21—C22	121.87 (17)	C32—C33—H33	119.8
C23—C22—C21	118.74 (18)	C33—C34—C35	119.96 (18)
C23—C22—H22	120.6	C33—C34—H34	120.0
C21—C22—H22	120.6	C35—C34—H34	120.0
C22—C23—C24	120.64 (18)	C34—C35—C36	120.16 (18)
C22—C23—H23	119.7	C34—C35—H35	119.9
C24—C23—H23	119.7	C36—C35—H35	119.9
C25—C24—C23	120.16 (18)	C35—C36—C31	120.32 (18)
C25—C24—H24	119.9	C35—C36—H36	119.8
C23—C24—H24	119.9	C31—C36—H36	119.8
C24—C25—C26	120.21 (18)	C12—O5—H5	109.5
C24—C25—H25	119.9	C21—O6—C13	121.00 (14)
C26—C25—H25	119.9		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O4	0.84	2.24	2.6680 (19)	112
O5—H5···O4^{i}	0.84	1.93	2.7022 (18)	153
C36—H36···O6	0.95	2.30	2.656 (2)	101
C32—H32···O5	0.95	2.19	2.852 (2)	126

Symmetry code: (i) $x-1/2, -y+3/2, -z+1$.